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Enhanced adsorption of crystal violet by synthesized and characterized chitin nano whiskers from shrimp shell

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ABSTRACT

Chitin nanowhiskers (ChNW) were extracted from shrimp shell and subjected to alkali, bleaching and acid hydrolysis treatment. The Fourier transform infrared (FTIR) spectra confirmed the functional group moieties present at each stage of the purification process. The X-ray diffraction (XRD) analysis determined the crystallinity of the ChNW. The scanning electron microscopic (SEM), transmission electron microscopic (TEM) and atomic force microscopic (AFM) studies were carried out to examine and compare the morphology of the products at each stage of purification. The synthesized ChNW were used for the crystal violet adsorption studies. Along with ChNW, a series of adsorbent materials like chitin-Fe_3O_4, cellulose, and cellulose – Fe_3O_4 were used for comparing the results and for the better understanding of adsorption phenomena. The absorbance of the solution during a time interval was investigated using UV–vis spectrophotometry. The prepared ChNW showed higher removal efficiency (79.13%) and adsorption capacity (39.56 mg g^{-1}) compared to other adsorbents. The results proved that ChNW can be a potential candidate for the removal of crystal violet from contaminated water.

1. Introduction

Environmental contamination by synthetic dyes is a serious problem due to their adverse ecotoxicological effects and bioaccumulation in the world. The dyes are organic colorant compounds that cause damage to the environment and harmful effects on the public health [1,2]. The textile, paper, plastics and dyestuffs industries consume substantial volume of water, inorganic and organic chemicals and dyes to color their products, which leads to considerable amount of contamination [3–7]. The primary source of aquatic pollution is toxic effluents from the above mentioned materials and they damage water sources [3]. Color is a first contaminant to be recognized in wastewater [7] which is highly visible and undesirable when water contains even little amount (less than 1 ppm for few dyes) of dyes [6].

Number of dyes are known to be toxic and even carcinogenic, and also caused serious damage to the environment [8]. A cationic dye, Crystal Violet also known as gentian violet with IUPAC name Tris(4-(dimethylamino)phenyl) methylium chloride is mostly used as a coloring agent. The intake of crystal violet by human beings causes harmful diseases like cancer [9] and higher concentration of crystal violet in water bodies leads to depletion of fresh water resources. It is also polluting our aqua systems and animals [8]. Hence removal of crystal violet from water bodies is a crucial issue to be given urgent attention.

Extensive research had been carried out for the removal and separation of dyes from contaminated water which included methods like adsorption [10], photo degradation [11], coagulation [12], ion exchange [13] and membrane filtrations [14]. Because of its simple procedure, cost effectiveness and higher performance, adsorption is found to be the most efficient method. Number of organic and inorganic adsorbents like clays [15], activated carbon [16], cellulose [17], carbon nanotubes [18], and magnetic oxides [19] bio wastes, by products from industries and natural materials like biopolymers were used for the removal of dyes in various studies. Pourjavadi et al. [20] have reported a very high crystal violet adsorption capacity of 769.23 mg g^{-1} by using graphene oxide based magnetic nanocomposite hydrogels and proved that graphene oxide had significant effect on the adsorption of crystal violet. Removal of crystal violet from aqueous solution using rice-husk based activated carbons was studied by Mohanty et al. [21] and reported that the materials were efficient for the adsorption of crystal violet. Asma et al. [22] studied the application of grape fruit peel for adsorbing crystal violet from the aqueous solution, and showed that grape

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Table 1
Specifications of crystal violet dye.

Generic name	C.I. Basic violet (10 BV 10)
Colour index number	42555
Abbreviation	10 (BV10)
Molecular formula	$C_2H_{30}N_3Cl$
Purity (%)	80
Molecular weight	408
I_{max}(nm)	584
Solubility in water	16 g/l (25A °C)

fruit peel was an effective adsorbent for the removal of crystal violet. The specifications of crystal violet used in the present study are given in Table 1.

Chitin, poly(β-(1-4)-*N*-acetyl-D-glucosamine) is a natural polysaccharide found in the exoskeleton of arthropods [23] and it is the second most abundant natural material in the world after cellulose [24]. Even though chitin occurs as two allomorphs namely α and β [25], α chitin is abundant, by available the cell wall of yeast, fungi, crab, shrimp and lobster shells and β chitin is rarely found in nature [26,27]. The chitin is usually considered as a structural materials and has a lesser important than other functional natural polymers such as proteins and nucleic acids [28]. However, with a better understanding of biological and physiological properties in recent years, the role of chitin is becoming more important, and the study of its application is of great interest [29].

ChNW are obtained from native chitin by acid hydrolysis, and considered as a very attractive class of nanomaterial with high surface to volume ratio and with hydroxyl and acetamide functional groups [30]. In the present study, ChNW were synthesized from shrimp shell, and a series of adsorbent materials like ChNW, ChNW with magnetic oxide (ChNWM) cellulose (C), cellulose with magnetic oxide (CM) were taken for comparative studies on the crystal violet adsorption.

2. Materials and methods

2.1. Materials

The shrimp shells were collected from the coastal areas of Kerala, South India and they were used for the extraction of chitin. The cellulose powder and magnetic oxide were obtained from Plant Lipids (Pvt) Ltd, Cochin, Kerala, India. Analar grade potassium hydroxide, sodium acetate, sodium hypochlorite and hydrochloric acid were purchased from Merck and were used without further purification. A mechanical stirrer of type IKA® T 25 digital ultra-turax, centrifuge machine and laboratory dialysis tubes obtained from Sigma-Aldrich were used.

2.2. Synthesis of ChNW

The method of preparation of ChNW was based on the study reported by Morin and Dufresne [31]. For the removal of proteins, the powdered shrimp shells were suspended in 5% aqueous potassium hydroxide solution for 6 h under boiling condition. Later, the residue was rinsed, filtered and kept at room temperature overnight under agitation. The obtained chitin was bleached with sodium hypochlorite solution (17 g of sodium hypochlorite in 1 L of 0.3 M sodium acetate buffer with pH 4.0) at 80 °C for 2 h. Subsequently, the washed residue was stored in 5% of potassium hydroxide for 72 h to remove the residual proteins. The resulting dispersion was hydrolyzed with hydrochloric acid, centrifuged and washed several times and the suspensions of ChNW were transferred to a dialysis bag and dialyzed until a pH of 6 was reached. The dispersion of ChNW was accomplished further by three successive ultrasonic treatment and filtration. Later, appropriate volume of hydrochloric acid solution was added to the suspension until the pH reached 2.5. A schematic experimental protocol used for the synthesis of ChNW is shown in Fig. 1.

2.3. Preparation of adsorbents

The adsorbents (ChNW and Cellulose) were prepared by the following method. The dispersion of ChNW (or) Cellulose was sonicated, subsequently cooled up to a temperature of 36 °C using isopropyl alcohol. After lyophilizing and freeze drying of frozen samples, a fine powder was obtained and used as adsorbent. The ChNW- magnetic oxide (ChNWM) mixture was prepared by taking 1 g of each of the powdered materials were mixing them for 3 h and it was directly used as an adsorbent. The cellulose -magnetic oxide (CM) mixture was also prepared by following the above procedure.

2.4. Morphology analysis

The morphology of chitin after various chemical treatments was observed using field emission scanning electron microscope (FE-SEM) (JEOL JSM-820 model) and atomic force microscope (AFM). Using FE-SEM, the effect of different chemical treatments was assessed by comparing native, treated and acid hydrolyzed chitin. All samples were dried in hot air oven at 60 °C for 12 h prior to experiments. The samples were coated with gold using a vacuum sputter to avoid subsequent charging before measurement. The accelerating voltage was 20 kV. For AFM analysis of ChNW, few milliliters of suspension were dropped in a silicon base and allowed to dry with the help of an infrared (IR) lamp. The surface of this film was analyzed with standard Si cantilever with a force constant of 10 N/m, a resonance frequency of 170 kHz and with a scanning rate of 1.0 Hz.

2.5. Fourier transform infrared (FTIR) analysis

FTIR was used to determine the functional moieties present in native, treated chitin and ChNW and it was recorded using a Shimadzu IR-470 IR spectrophotometer. Prior to experiment, all samples were dried in an air oven at 60 °C for 12 h. The FT-IR spectra for each sample were obtained over the wavelength ranging from 400 to 4000 cm^{-1}. The potassium bromide disk (ultra-thin pellets) method was used, and the experiments were carried out with a resolution of 2 cm^{-1} and a total of six scans conducted for each sample.

2.6. X-ray diffraction (XRD) analysis

XRD technique was used to determine the crystallinity of chitin after various chemical treatments. The materials in the form of powder were placed in the sample holder and leveled to obtain total and uniform X-ray exposure. The X-ray equatorial diffraction patterns of native, treated chitin and ChNW were achieved with an X-ray diffractometer (Bruker Diffractometer D8 Advance Model) using CuKα radiation ($\lambda = 1.5406$ Å) at the operating voltage and current of 40 kV and 40 mA respectively. The X-ray diffraction pattern was obtained at room temperature with 2θ from 5 to 60°,and with a scan rate of 2° min^{-1}.The crystallinity index (I_{cr}) of all materials was determined by the Segal method as shown in the Eq. (1) [32].

$$I_{cr} = \frac{I_{002} - I_{am}}{I_{002}} X100 \qquad (1)$$

Where I_{cr} expresses the relative degree of crystallinity, I_{002} is the maximum intensity of the (002) lattice diffraction at $2\theta = 22°$, and I_{am} is the intensity of diffraction at $2\theta = 18°$. I_{002} represent both crystalline and amorphous regions while I_{am} represent only the

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